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Paleolimnological assessment of riverine and atmospheric pathways and sources of metal deposition at a floodplain lake (Slave River Delta, Northwest Territories, Canada)

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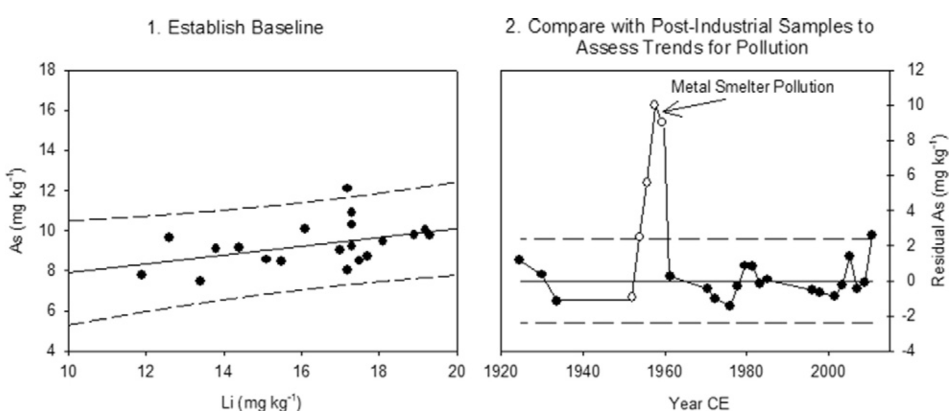
HIGHLIGHTS

- We examine metal depositional history at a floodplain lake in the Slave River Delta.
- No evidence of metal enrichment in sediment record since onset of oil sands development
- Evidence of As enrichment during 1950s likely from Giant Mine emissions
- Floodplain lakes archive records of contaminant deposition by air and water
- Knowledge of paleohydrology & pre-disturbance baseline key to detecting pollution

GRAPHICAL ABSTRACT



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ABSTRACT

Growth of natural resource development in northern Canada has raised concerns about the effects on downstream aquatic ecosystems, but insufficient knowledge of pre-industrial baseline conditions continues to undermine ability of monitoring programs to distinguish industrial-derived contaminants from those supplied by natural processes. Here, we apply a novel paleolimnological approach to define pre-industrial baseline concentrations of 13 priority pollutant metals and vanadium and assess temporal changes, pathways and sources of these metals at a flood-prone lake (SD2) in the Slave River Delta (NWT, Canada) located ~500 km north of Alberta's oil sands development and ~140 km south of a former gold mine at Yellowknife, NWT. Results identify that metal concentrations, normalized to lithium concentration, are not elevated in sediments deposited during intervals of high flood influence or low flood influence since onset of oil sands development (post-1967) relative to the 1920–1967 baseline established at SD2. When compared to a previously defined baseline for the upstream Athabasca River, several metal-Li relations (Cd, Cr, Ni, Zn, V) in post-1967 sediments delivered by floodwaters appear to plot along a different trajectory, suggesting that the Peace and Slave River watersheds are important natural sources of metal deposition at the Slave River Delta. However, analysis revealed unusually high concentrations of As deposited during the 1950s, an interval of very low flood influence at SD2, which corresponded closely with emission history of the Giant Mine gold smelter indicating a legacy of far-field

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atmospheric pollution. Our study demonstrates the potential for paleolimnological characterization of baseline conditions and detection of pollution from multiple pathways in floodplain ecosystems, but that knowledge of paleohydrological conditions is essential for interpretation of contaminant profiles.

1. Introduction

As resource development has increased in northern Canada, so too have concerns regarding effects of associated pollutants on environmental and human health (e.g., Arctic Monitoring and Assessment Programme, 1998; Schindler, 2010). Determining the extent of pollution can be complicated because many contaminants of concern, including organic pollutants, heavy metals and radioactive substances, may come from a variety of industrial sources (CACAR, 2003), and they can be transported to northern communities and ecosystems by multiple pathways including via air and water. Further complexities may arise for those communities and ecosystems that are located near to where natural sources of these contaminants are also present (e.g., Bacardit et al., 2012; Hall et al., 2012; Jautzy et al., 2015; Wang et al., 2015). Unfortunately, environmental monitoring programs are often initiated long after resource development has already begun (Blais et al., 2015a). Without knowledge of pre-industrial baseline or reference conditions, it is difficult or impossible to distinguish industrial-derived pollutants and their pathways from those contaminants that may be supplied from natural sources and processes of transport acting within the watershed (e.g., Kersten and Smedes, 2002; Bowman and Somers, 2005; Hawkins et al., 2010; Blais et al., 2015a,b).

The Slave River Delta (SRD), Northwest Territories, is an important floodplain landscape located downstream and downwind of major resource developments (Fig. 1). Here, concerns of the local community have been growing regarding the potential far-field effects of oil sands mining activities in northern Alberta (Campbell and Spitzer, 2007; Wesche, 2007, 2009; AANDC and ENR-GNWT, 2012). In fact, the region that includes the Slave River and SRD is part of Environment Canada's 'Phase 2' Integrated Monitoring Plan for the Oil Sands in recognition of the possibility for far-field transport and accumulation of oil sands contaminants (Environment Canada, 2011). Developing knowledge of pre-industrial baseline conditions has been identified as a major research priority to improve the effectiveness of monitoring in the oil sands region (Dowdeswell et al., 2010).

As part of an initiative led by the Slave River and Delta Partnership [http://www.nwtwaterstewardship.ca/node/74], we launched a paleolimnological project to assess the nature of deposition of polycyclic aromatic compounds (PACs; Elmes, 2013) and metals (this study) at the SRD, building on the success of similar studies at the Peace-Athabasca Delta (PAD; Hall et al., 2012; Wiklund et al., 2012, 2014). Although paleolimnological results from the PAD suggested that both fluvial and airborne pollution from industrial development of the oil sands are unlikely to reach the more distant SRD (Hall et al., 2012; Wiklund et al., 2012, 2014), no knowledge exists of baseline conditions of contaminant deposition in the SRD. Nor is there knowledge of whether oil sands and other sources of contaminants derived from *natural processes* occurring upstream along the Athabasca, Peace and Slave rivers are present in the delta. Over 100 km of the Athabasca River and its tributaries contain shoreline exposures of the bitumen-rich McMurray Formation. Natural erosion of these strata was identified as the overwhelming source of 'river-transported bitumen-associated' PACs that are deposited in floodplain lake sediments of the Athabasca Delta (Hall et al., 2012). And, the Peace River has also been identified as a source of natural, petrogenic PACs supplied to the northern Peace sector of the PAD (Jautzy et al., 2015). During the course of the present study, we also recognized that pollutants from other northern resource developments may be contained in SRD lake sediments, including arsenic (As) from gold smelting emissions at Giant Mine near Yellowknife (Fig. 1).

In the absence of direct measurements, paleolimnological investigations offer one of the very few methods to establish baseline conditions for contaminants in aquatic ecosystems, which are necessary to identify pollution from industrial activity (e.g., Kurek et al., 2013; Blais et al., 2015a,b; Boyle et al., 2015). Indeed, time-series records of contaminants in lake sediments have long been successfully applied to assess pollution from a variety of sources and to determine pathways of deposition (e.g., Thomas, 1972; Bindler et al., 2011; Tapia et al., 2012; Wei and Wen, 2012; Catalan et al., 2013; Boyle et al., 2015; Catalan, 2015; Cooke and Bindler, 2015). For example, this approach has been used to assess near- and far-field industrial pollution supplied to lakes via the atmosphere (e.g., Cooke and Abbott, 2008; Muir et al., 2009), and from point source (e.g., mine tailings, pulp mills) discharges within the local catchment (e.g., Boyle et al., 2015; Dahmer et al., 2015). Paleolimnological assessments of river pollution have also been conducted, but mainly from sediments archived in riverine lakes and reservoirs (e.g., Foster and Charlesworth, 1996; Balogh et al., 1999, 2009; Audry et al., 2004).

Deltas are hydrologically-complex landscapes but have the potential to record and archive, in their floodplain lake sediments, contaminants that are derived from multiple pathways. Varying influences of hydrological processes and their effects on lacustrine stratigraphic records can complicate interpretation of contaminant profiles (e.g., Rosen, 2015), and this may explain why floodplain lakes have been relatively underutilized. Yet, knowledge of floodplain lake paleohydrology has demonstrated to be a powerful tool for extracting information about contaminant deposition over time via both fluvial and atmospheric vectors. For example, in the PAD, Hall et al. (2012) used lowland floodplain lake sediment records to examine PAC deposition delivered by river floodwaters during high flood influence intervals before and after onset of oil sands development, and Wiklund et al. (2012) used an upland lake sediment record beyond the reach of river floodwaters to reconstruct temporal changes in atmospheric deposition of metals to the area.

Here, we utilize a detailed pulse-flood record from a lake in the SRD to improve knowledge of metal deposition via fluvial processes from analysis of sediment intervals deposited during periods of high flood influence *and* metal deposition by atmospheric transport from analysis of sediment intervals deposited during periods of low flood influence. We incorporated the data handling approaches described by Wiklund et al. (2014), which includes normalizing metal concentrations to Li to account for expected variations in grain size and mineralogy (Loring, 1991; Kersten and Smedes, 2002) that occur over time and space in deltas and other depositional environments with widely varying hydrological conditions. We apply this method to establish baseline concentrations of metals, assess temporal patterns of change in relation to depositional processes and pathways, and determine whether there is evidence of pollution from resource development to this remote northern landscape.

2. Methods

2.1. Study site

The SRD is a large floodplain landscape (~400 km^2) with abundant forests, channels, wetlands and small lakes that span broad hydrological gradients and provide important habitat for a diverse array of wildlife and resources, and which support the traditional lifestyle of the mainly First Nation community of Fort Resolution (English et al., 1997; Brock

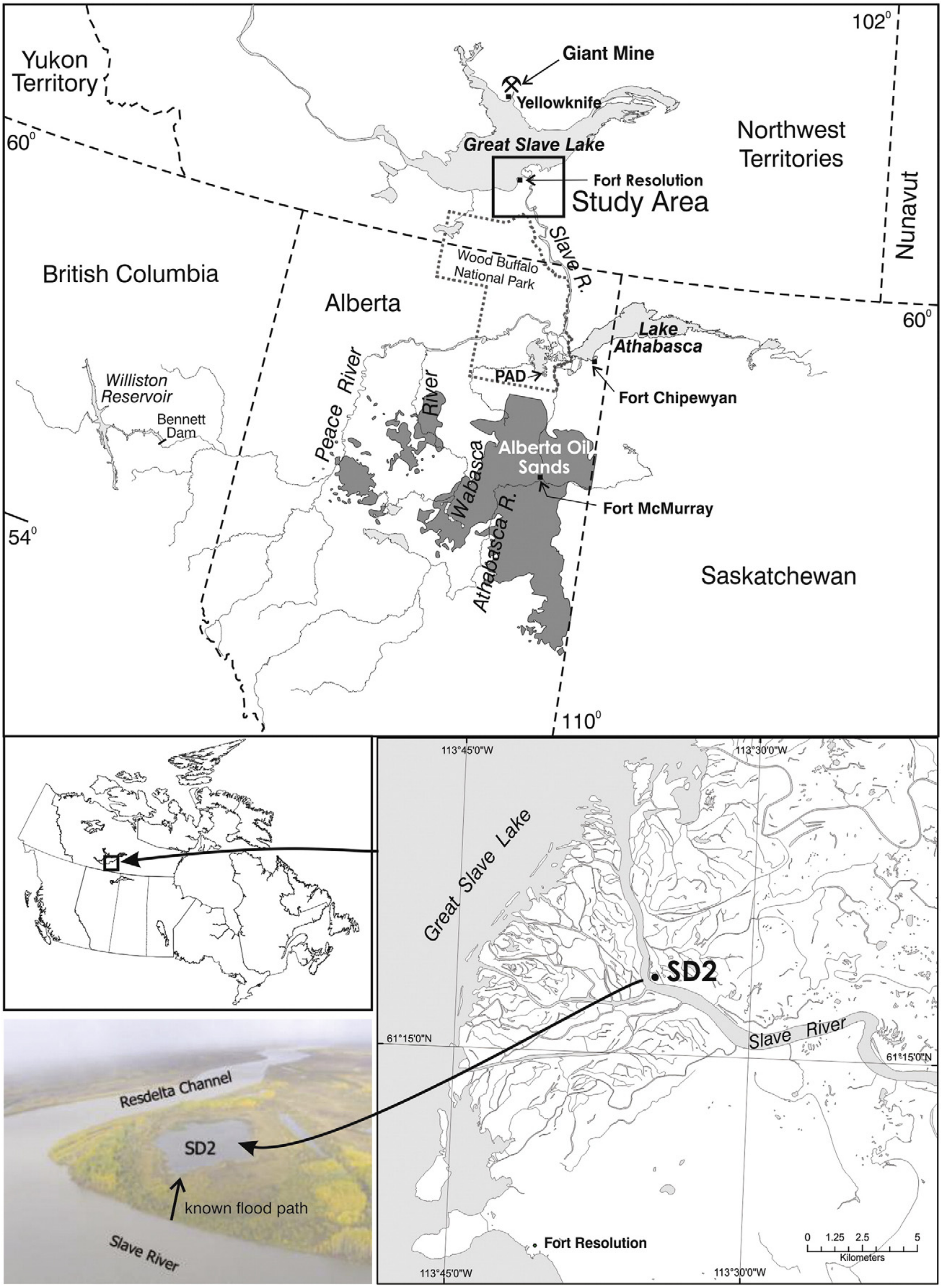

Fig. 1. Maps and photo showing the Slave River Delta (Northwest Territories, Canada) and the study lake (SD2). The Slave River Delta is located downstream of the Alberta oil sands development and downwind of Giant Mine, a former gold mine near Yellowknife, NWT.

et al., 2007; Sokal et al., 2008). The SRD has formed in response to deposition of sediment by the Slave River where it enters Great Slave Lake. The Slave River originates north of the PAD where the Peace River and Rivière des Rochers meet in northern Alberta and its watershed includes the Peace and Athabasca rivers (Fig. 1). Approximately two-thirds of annual Slave River discharge is derived from the Peace River and the remaining third comes from other north-flowing tributaries in the PAD, including Rivière des Rochers, Revillon Coupé, and Chenal des Quatre Fourches, which carry flow from the Athabasca River and Lake Athabasca (English et al., 1997). The prevailing winds in the SRD region are from the northwest (Gardner et al., 2006).

In this study, we utilize the recent (post-1920s) sediment record from lake 'SD2' (61°16′56.21″N, 113°34′55.51″W), which is a small (~1.2 km^2), shallow (maximum depth ~ 1.5 m) flood-dominated lake in the SRD (Fig. 1). SD2 is pivotally located at a sharp bend in the Slave River at the entry point to the active delta before it divides into multiple distributary channels, making the lake prone to receive river floodwaters during spring ice-jam events. For example, in May 2005 we observed a substantial amount of fluvial sediment in the lake's catchment freshly deposited by overbank flooding caused by an ice-jam event on the Slave River. Prior paleolimnological studies using a diverse set of indicators revealed SD2 contains a detailed record of 20th century Slave River flood history that corresponds well with temporal patterns evident in river discharge data and with local traditional knowledge of flood events (Brock et al., 2010).

2.2. Sediment core collection

A 48-cm long sediment core was retrieved from SD2 in September, 2011 using a Glew (1998) gravity corer fitted with a Lucite tube (7.62 cm inner diameter). The core was transported to Deninu School in Fort Resolution and sectioned into 1.0-cm intervals using a vertical extruder (Glew, 1998). All samples were sealed in Whirl-Pak® bags and stored in the dark at 4 °C during shipping and until analysis.

2.3. Sediment core analyses

Knowledge gained from Brock et al. (2010) was used to inform our sediment dating approach. In this prior study, high sedimentation rates resulted in low ^{210}Pb activity, making this technique ineffective for establishing the sediment core chronology. However, a distinctive peak in ^{137}Cs was identified in the stratigraphic record, considered to represent the 1963 peak of maximum atmospheric fallout (Appleby, 2001), and was thus used to estimate a linear sedimentation rate. Based on these results, freeze-dried sediment samples from the new sediment core from SD2 were analyzed for ^{137}Cs using an Ortec coaxial HPGe Digital Gamma Ray Spectrometer (Ortec #GWL-120-15) interfaced with Maestro 32 software (version 5.32) at the University of Waterloo Environmental Change Research (WATER) Laboratory.

Brock et al. (2010) explored the use of multiple paleolimnological methods for reconstructing flood history from the SD2 lake sediment record, and found that C/N ratios provided an effective measure that was consistent with river discharge data and local traditional knowledge. High C/N ratios were interpreted to represent influx of terrestrial organic matter delivered by flood events, whereas low C/N ratios occurred due to greater supply of autochthonous organic matter during intervals of low flood influence. This interpretation was supported by a high C/N ratio measured in flood-derived sediment collected on land near the lake's shoreline immediately after river flooding in spring of 2005. To determine C/N ratios, bulk organic carbon and nitrogen concentrations were measured on every 1-cm sediment interval of the core from SD2 at the University of Waterloo Environmental Isotope Laboratory, following the methods of Wolfe et al. (2001). The analytical uncertainty for organic carbon and nitrogen elemental composition, based on sample repeats, was ±0.21% and ±0.02%, respectively.

For metal analyses, subsamples of freeze-dried sediment from every 1-cm interval in the core were analyzed at ALS Canada Ltd. (Edmonton) following the method EPA 200.2/6020A and EPA 200.2/245.7 (total Hg). Metals that we report results for include the 13 priority pollutants under the US Environmental Protection Agency's Clean Water Act (antimony [Sb], arsenic [As], beryllium [Be], cadmium [Cd], chromium [Cr], copper [Cu], lead [Pb], mercury [Hg], nickel [Ni], selenium [Se], silver [Ag], thallium [Tl] and zinc [Zn]), as well as vanadium (V), a key metal of concern associated with the Alberta oil sands (Jacobs and Filby, 1982; Reynolds et al., 1989; Gosselin et al., 2010). As explained below, we also report lithium (Li) for the purposes of normalizing metal concentrations to expected variations in grain size and mineralogy (Loring, 1991; Kersten and Smedes, 2002).

2.4. Stratigraphic and numerical analyses

To assess temporal changes in metal concentrations in the SD2 sediment core, we first explored stratigraphic patterns in relation to intervals of high and low flood influence. Then, we followed normalization approaches outlined by Wiklund et al. (2014) to account for the expected negative correlation of grain size and metal concentration (Loring, 1991; Kersten and Smedes, 2002), because SD2 is subject to varying hydrological conditions. Geochemical normalization was chosen over granulometric methods as research has shown that it is superior because it can account for both mineralogical and granular variability (Loring, 1991). We explored the use of Al and Li as normalizers, which are both commonly used in aquatic sediments. We selected Li as the normalizer in this study for two reasons. First, Loring (1990, 1991) indicates that Li is equal or superior to Al for normalization of metal concentrations in aquatic sediments. Second, after examining our data, the results were equivalent for Al and Li, but the linear relationships for several metals were stronger with Li than with Al.

To assess potential for metal pollution in SD2 sediments from the oil sands development, we assumed Slave River floodwaters are the predominant pathway, because evidence indicates atmospheric supply of contaminants has not become elevated at the PAD, which is located ~300 km closer to the mining activity (Hall et al., 2012; Wiklund et al., 2012; Kirk et al., 2014). First, we developed linear relations for pre-1967 (year commercial oil sands development began; Gosselin et al., 2010) lake sediment metal concentrations relative to Li concentration using samples deposited during intervals of high flood influence (Fig. 2). And, we established 95% prediction intervals (PI) about these relations to define the natural range of variation in normalized metal concentrations in sediments supplied by the Slave River (i.e., pre-oil sands development). Due to the possibility of multiple sources of metals (e.g., eroded from metal-bearing deposits along the Athabasca and Peace rivers), we did not force regressions through the origin, as is commonly done when only one source is expected (e.g., Loring and Rantala, 1992; Wiklund et al., 2014). Second, we evaluated post-1967 sediment metal concentrations (i.e., since onset of oil sands development) for samples within high flood influence intervals against the baseline constructed from the pre-1967 intervals of high flood influence. We also assessed metal concentrations during intervals of low flood influence against the pre-1967 baseline because of the possibility that flood-derived sediment in SD2's local catchment may be subsequently mobilized and deposited in the lake by snowmelt and rainfall runoff. If >2.5% of post-1967 lake sediment samples fall above the upper 95% PI, this identifies an additional source of the metal (Loring, 1991; Kersten and Smedes, 2002), possibly due to oil sands pollution. Third, we re-expressed these data as time-series plots of 'residuals' about the metal-Li relation, which provides an ability to assess temporal trends of past *and* ongoing monitoring data relative to the baseline (residual = 0) (see Wiklund et al., 2014). In these 'residual plots', we used linear extrapolation of the widest PI for the pre-1967 samples as a benchmark to assess for pollution, as described in Wiklund et al. (2014).

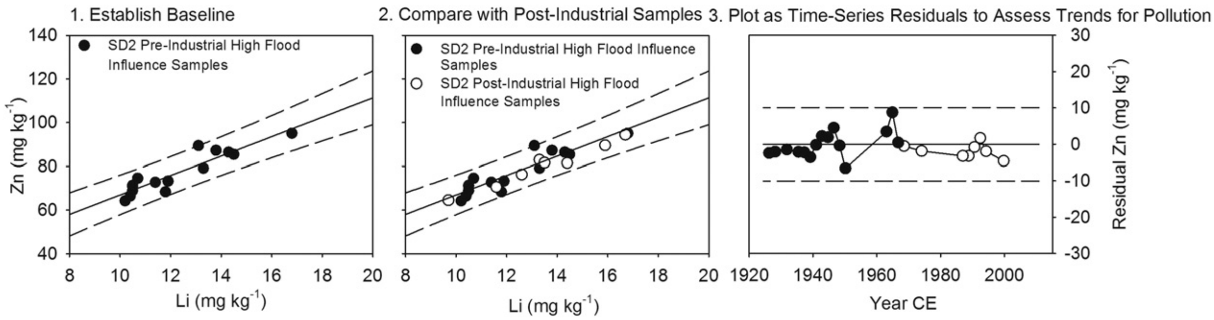

Fig. 2. Schematic diagram showing the three-step approach to assess metal pollution (e.g., zinc) from analyses of pre-industrial sediments supplied by floodwaters to flood-prone lakes.

Emissions from the smelting activities at Giant Mine increased rapidly beginning in the 1950s and then decreased rapidly after this decade following implementation of emission control measures (Hocking et al., 1978). To assess potential for As pollution from Giant Mine during the 1950s, we modified the methods described above (and in Fig. 2) because transport of Giant Mine pollution to the SRD would be primarily by atmospheric pathways, and the evidence of pollution would be best captured in the stratigraphic record during times of reduced river flooding rather than in sediments deposited at times of frequent flooding (i.e., during times when atmospheric delivery was less diluted by fluvial delivery processes). To do this, we developed baseline As–Li relations and PIs based on pre-1950s and post-1960s samples deposited during intervals of low flood influence. The 1950s was an interval of low flood influence in the SD2 stratigraphic record and As data from this interval were examined against the low flood influence As–Li baseline, and then subsequently re-expressed as a time-series plot of residuals about the As–Li relation.

3. Results

3.1. Paleohydrological context

Peak ^{137}Cs activity (0.021 Bq g^{-1}) occurred at 26.5 cm and was interpreted to represent 1963 (Fig. 3), the year of maximum atmospheric fallout (Appleby, 2001). The peak activity was equivalent to that reported in Brock et al. (2010). Using this stratigraphic horizon, the estimated linear sedimentation rate (0.54 cm $yr.^{-1}$) was similar to that derived by Brock et al. (2010; 0.62 cm $yr.^{-1}$). Extrapolation down-core resulted in a basal date of ~1924. During intervals of low flood influence, the linear sedimentation rate is likely an overestimate, and vice versa during intervals of high flood influence.

As reported by Brock et al. (2010), high C/N ratios in the sediment core record reflect intervals of high flood influence, which was further supported by the high C/N ratio (15.9) measured in the 2005 flood deposit sampled from the lake's shoreline. On this basis, we interpret the following intervals to reflect high flood influence in the new sediment core: ~1926–1928 (46–45 cm), ~1931 (43 cm), ~1935–1950 (41–33 cm), ~1963–1968 (26–23 cm), ~1974 (20 cm), ~1986–1994 (13–9 cm) and ~1999 (6 cm) (Fig. 4). Intervals of low flood influence include ~1924 (47 cm), ~1930 (44 cm), ~1933 (42 cm), ~1952–1961 (32–27 cm), ~1970–1972 (22–21 cm), ~1975–1985 (19–14 cm), ~1996–1998 (8–7 cm) and ~2001–2011 (5–0 cm). These intervals of high and low flood influence are similar to the previously published record from SD2 (Brock et al., 2010). Notably, the interval from ~1952–1961 has the lowest C/N ratios in the stratigraphic record. Brock et al. (2010) identified that lake levels during this interval were extremely low (5–15 cm) based on the presence of *Sagittaria cuneata* seeds, a consequence of an extended period with minimal influence of Slave River flooding.

3.2. Temporal patterns of metal concentrations

The stratigraphic profiles for the 13 priority pollutant metals and V show prominent temporal variations, and are largely mirror images to that of the C/N profile (Fig. 4). Stratigraphic intervals with high C/N ratios (i.e., high flood influence) typically have relatively low concentrations of metals and, conversely, stratigraphic intervals with low C/N ratios (i.e., low flood influence) tend to have relatively high concentrations of metals. Peak concentrations for the majority of metals occur during the late 1950s (low C/N ratios, low flood influence), which is especially evident in the As profile. In contrast, lowest metal concentrations occur during the late 1930s, 1940s and 1990s, which are intervals of high flood influence. Independent sample t-tests show that concentrations of all metals, except As, are significantly higher (at alpha = 0.05) in sediments deposited post-1967 onset of oil sands development compared to those deposited pre-oil sands development. However, our analyses of the core from SD2 included a greater number of low flood influence samples after 1967 (16) than before 1967 (9), which confounds the comparison because hydrological control of grain-size variations likely exert strong

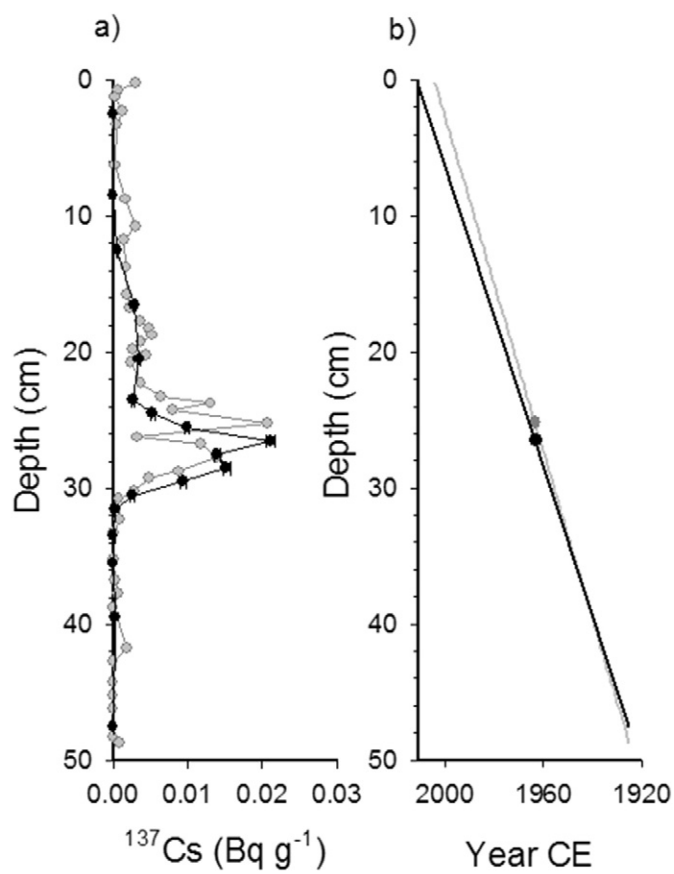

Fig. 3. Panel a) presents the ^{137}Cs activity profile and panel b) presents the — estimated age–depth relationships and sediment core chronologies for SD2 from both the 2004 core from Brock et al. (2010) (gray symbols and solid gray lines) and the core collected in 2011 for this study (black symbols and solid black lines).

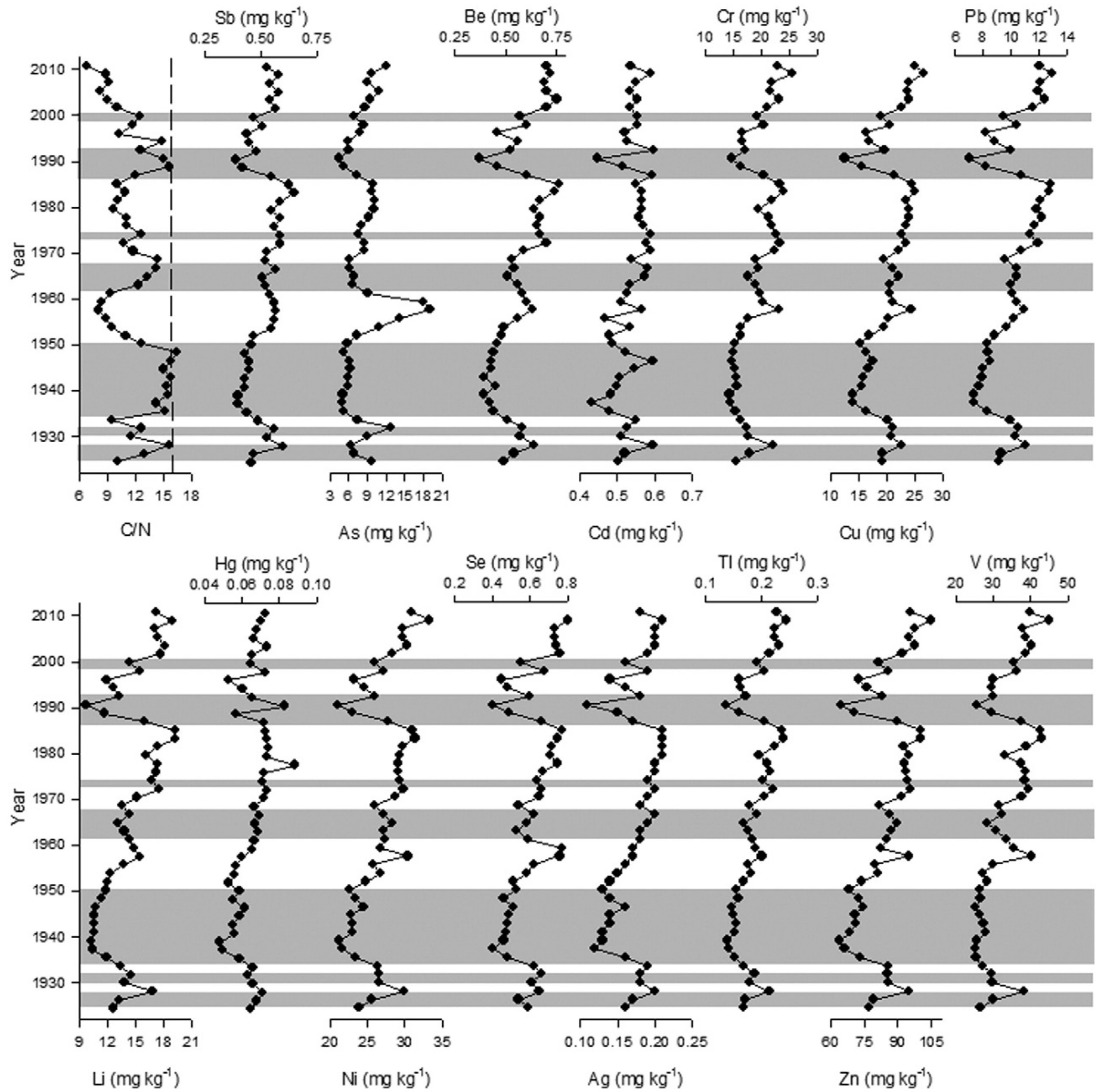

Fig. 4. Stratigraphic profiles for the ratio of organic carbon-to-nitrogen concentration (C/N) and concentrations of 13 priority pollutant metals, vanadium and lithium. Gray horizontal shading indicates intervals of high flood influence based on the C/N ratio, whereas absence of shading indicates intervals of low flood influence. The vertical dashed line in the C/N profile represents the C/N ratio of Slave River sediment sampled within the catchment of SD2 after a spring flood event in 2005 (Brock et al., 2010).

influence on sediment metal concentrations, and highlights the need for normalization (see next section).

3.3. Assessment of metal pollution

To assess whether pollution is evident since onset of oil sands development, baseline concentrations normalized to Li were determined from pre-1967 samples within C/N-ratio defined high flood influence intervals (Fig. 5). In these samples, all metals show strong linear relations with Li (average $r^2 = 0.801$, not including As; As–Li $r^2 = 0.217$, see below). Post-1967 metal concentrations from high flood influence intervals tightly cluster along the regression lines, overlap with the pre-1967 data, and plot within the 95% PIs established from pre-1967 high flood influence intervals, with the exception of two analyses (Be, Hg; Fig. 5). Metal concentrations from post-1967 low flood influence intervals show similar distributions, with five values positioned above the 95% PI (Cr, Hg, Se and two for V) and one value positioned right on the 95% PI (Be). Distributions of pre-1967 metal concentrations from low flood influence intervals tend to be well characterized by the relation established for the pre-1967 high flood influence intervals, with the exception of several As concentrations. Notably, metal concentrations from low flood influence intervals tend to plot along the higher end of the regression lines, which reflects the expected relation between low energy hydrological conditions and preferential association of metals with fine-grained sediments.

To better visualize the timing of when Li-normalized metal concentrations exceeded the upper 95% PI, the residuals (i.e., the vertical distances of metal concentrations from the metal-Li regression line) were plotted in a temporal sequence (Fig. 6). During the post-1967 oil sands development era, two analyses from the high flood influence intervals (Be in ~1994 and Hg in ~1990) and six analyses from the low flood influence intervals (Be in ~2003, Cr in ~1970, Hg in ~1977, Se in ~2011, V in ~1970 and ~2009) exceed the upper 95% PI. These eight exceedances represent 2.38% of total metal analyses in samples

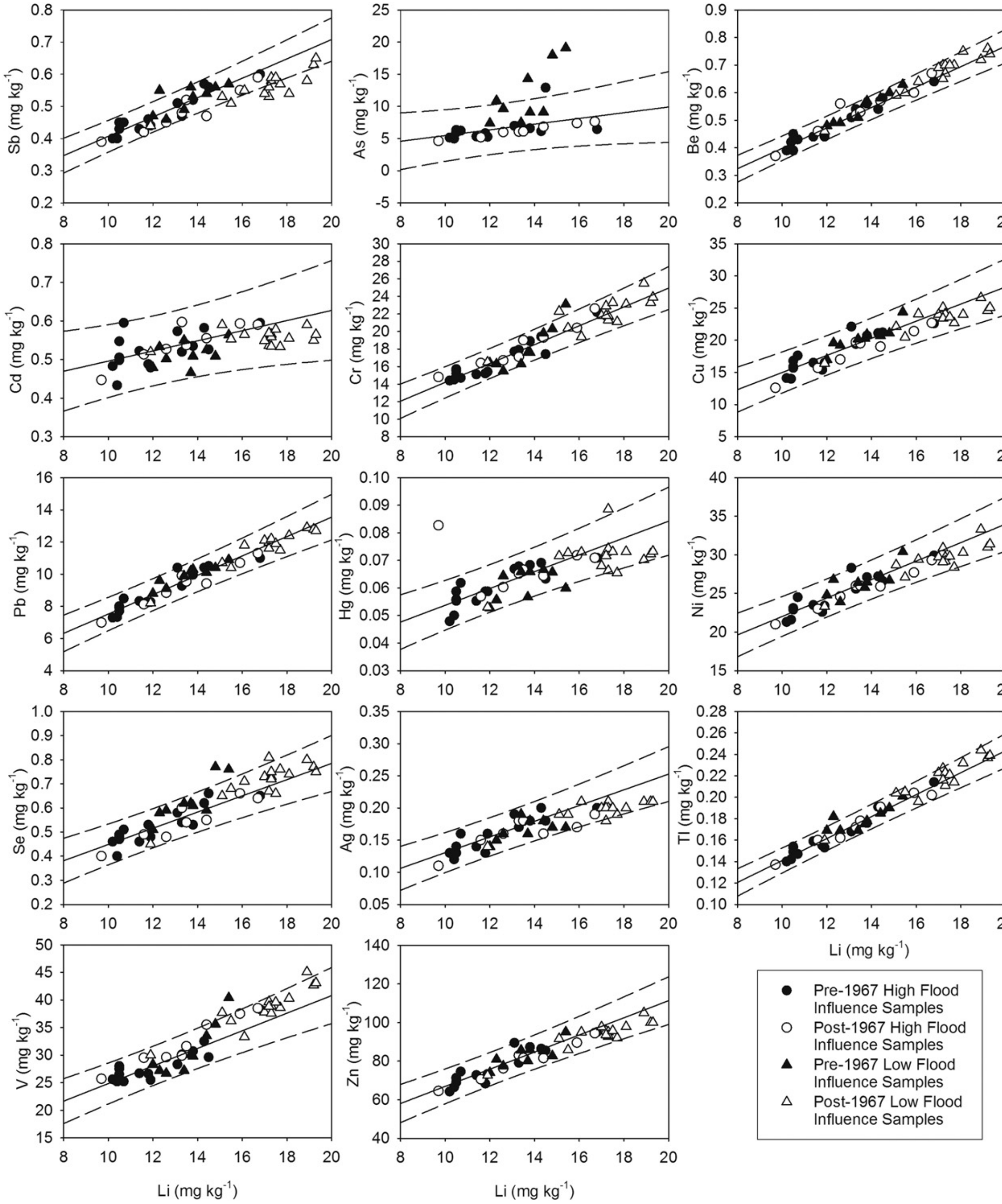

Fig. 5. Scatterplots showing regressions of metal concentrations versus lithium concentration. Linear regressions (solid lines) and 95% prediction intervals (dashed lines) based on sediments deposited pre-1967 during intervals of high flood influence.

deposited since onset of oil sands development (n = 336), which provides little to no evidence that they have been enriched by pollution from oil sands development or other sources. On the other hand, it was more common for the residual values of metals to exceed the 95% PI in low flood influence samples deposited during the 1950s *prior* to the oil sands development era, especially for As (but also Sb, Cr, Se, Tl and V). This observation, combined with prior knowledge that this decade was characterized by extremely low flood influence (Brock et al., 2010), suggests that a pathway of contaminant transport other than by river flooding may have been important during this time — namely via the atmosphere.

To explore further the high sediment As concentrations during the 1950s, we determined the atmospheric baseline for As–Li from the linear relation and PIs derived from low flood influence samples deposited pre-1950 and post-1960 (Fig. 7). Based on this relation, four of the five samples deposited during the 1950s contain unusually high As concentrations (i.e., exceeded the upper PI in ~1954, ~1955, ~1957 and ~1959). The As concentrations in these samples are above the Threshold

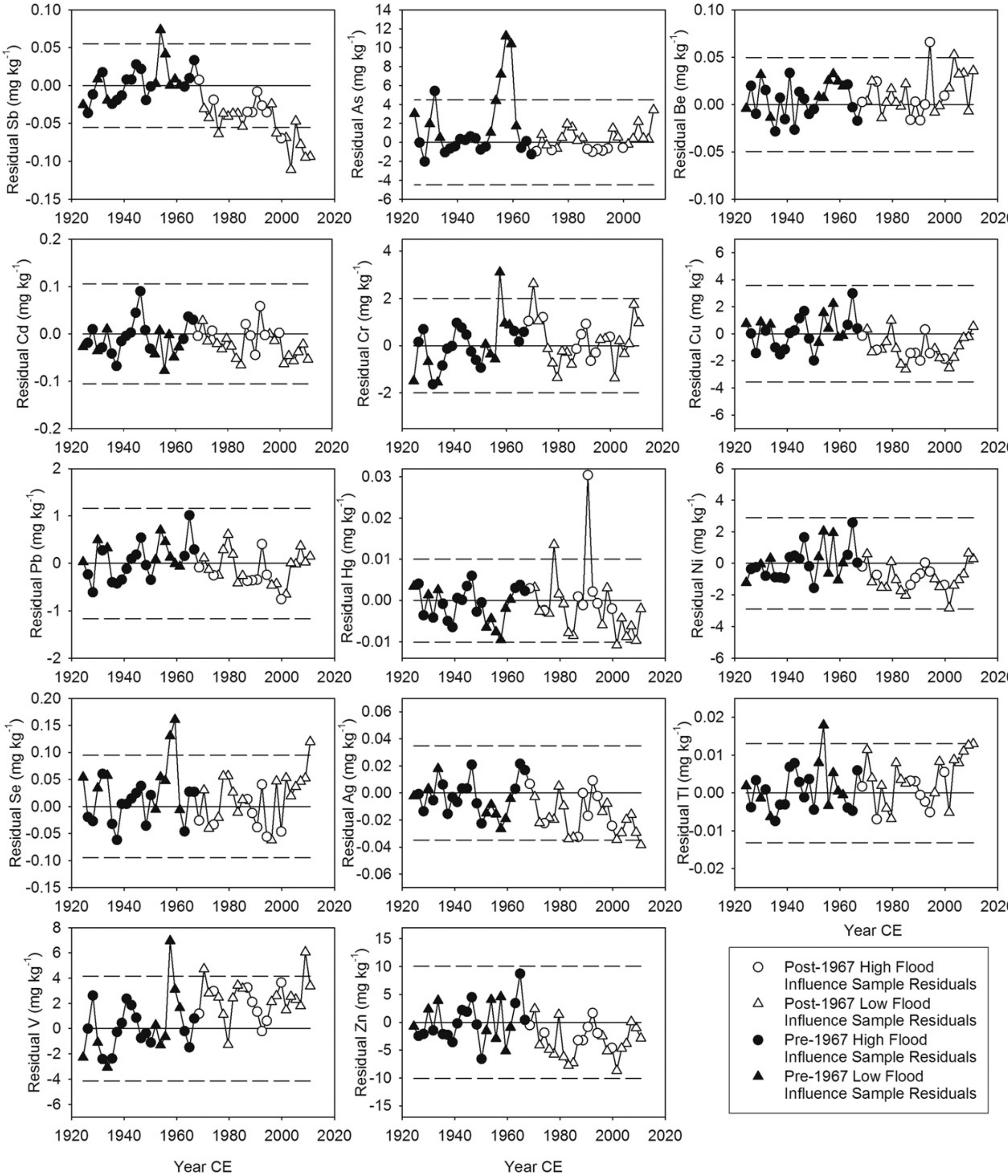

Fig. 6. Time-series plots showing temporal patterns of change in residual metal concentrations from the Li-normalized pre-1967 baseline based on sediments deposited at lake SD2 during intervals of high flood influence (horizontal solid line at 0). Dashed lines represent the widest 95% prediction interval from the pre-1967 high flood influence data.

Effects Level (5.9 mg kg^{-1}; CCME, 2014) and samples deposited in ~1957 and ~1959 exceeded the Probable Effects Level (17.0 mg kg^{-1}; CCME, 2014), which we attribute to far-field emissions from gold smelting at Giant Mine, as further discussed below.

4. Discussion

Knowledge of paleohydrological conditions was a critical first step in deconstructing pathways and sources of contaminant deposition at the study lake, SD2. While the sediment records of floodplain lakes have not been extensively exploited for this purpose, we show that they have potential to archive baseline conditions from multiple vectors, which can be used to detect evidence of pollution.

4.1. Processes and pathways of metal deposition at SD2

Metal concentrations in the stratigraphic record from lake SD2 show marked fluctuations associated with variations in paleohydrological conditions, yet the apparent relations may seem counterintuitive given that river floodwaters are a potential source of contaminant supply. Relatively high sediment metal concentrations are associated with intervals of *low* flood influence, whereas lower concentrations are present in intervals of *high* flood influence. This inverse relationship contrasts with

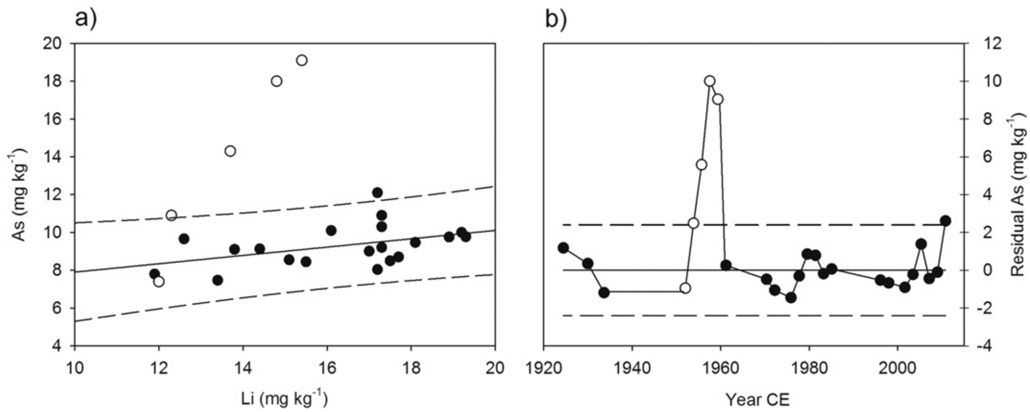

Fig. 7. Panel a) shows a scatterplot of arsenic concentration versus lithium concentration in sediments deposited in lake SD2 during intervals of low flood influence pre-1950 and post-1960 (black circles). The linear regression (solid line) and 95% prediction intervals (dashed lines) are shown. Open circles are from the low flood influence interval of the 1950s. Panel b) shows a re-expression of these data as time-series plots of 'residuals' about the As–Li relation to assess temporal patterns of arsenic pollution above the pre-1950 and post-1960 low flood influence baseline (horizontal solid line at 0). Dashed lines represent the widest 95% prediction interval.

delivery of 'river-transported bitumen-associated' PACs to lakes 'PAD23' and 'PAD31' in the Athabasca Delta, where flood deposits were enriched in these contaminants compared to lacustrine sediments deposited in the absence of flooding (Hall et al., 2012), but is consistent with variations of 'river-transported bitumen-associated' PACs in the SD2 stratigraphic record (Elmes, 2013). Evidently, sediment-laden floodwaters from the Slave River that enter SD2 are relatively diluted in metals and organic contaminants in comparison to Athabasca River floodwaters that enter PAD23 and PAD31 at the Athabasca Delta. Although contributions of contaminant-poor sediment from the Peace River may account for these differences, SD2 may simply receive a greater proportion of coarser-grained sediment during flood events that has relatively lower concentration per mass of sediment in comparison to finer-grained sediment that enters PAD23 and PAD31 during Athabasca River flood events. Supporting this notion is that SD2 is located immediately adjacent to the Slave River and, thus, likely receives higher-energy flows in comparison to the more 'off-line' hydrological settings of lakes PAD23 and PAD31. Relatively higher metal concentrations during low flood influence intervals in the SD2 sediment record may reflect finer-grained flood-derived sediment with relatively higher metal concentration per unit mass that was stored on the lake's catchment and re-mobilized during spring snowmelt or intense rain runoff events. Thus, sedimentation during intervals of low flood influence may not be entirely autogenic, as is also suggested by the low organic content throughout the core. Studies of additional lake sediment core records in the SRD along a gradient of flood intensity are required to further disentangle the influence of hydrological processes on floodplain metal stratigraphy. Clearly, however, these relations demonstrate that knowledge of paleohydrological conditions is crucial to the interpretation of the depositional history of metals at SD2, as has also been demonstrated at lakes in the PAD (Hall et al., 2012; Wiklund et al., 2012) and in other similar studies of floodplain and delta lakes in Europe (Foster and Charlesworth, 1996; Audry et al., 2004; Schulz-Zunkel and Krueger, 2009). Although most of the variation in metal concentrations in the stratigraphic profile from SD2 can be explained by river floodwaters and their likely influence on grain size and associated metal content, paleohydrological knowledge was also key to inform that enrichment of some metals, most notably As (but possibly also Sb, Cr, Se, Tl and V), likely occurred via atmospheric pathways during the 1950s.

In the absence of direct measurements, paleolimnological records of contaminant concentrations in locations where there are natural sources of contaminants provide unique opportunity to characterize baseline conditions and inherent, natural variation in the deposition of contaminants (Blais et al., 2015a,b; Boyle et al., 2015). In the pulse-flood stratigraphic record of SD2, we utilized high flood influence intervals to define baseline concentrations of metals delivered by Slave River floodwaters prior to the onset of oil sands development *and* we used low flood influence data prior to 1950 and after 1960 to define baseline concentrations of metals delivered by atmospheric pathways and detect deposition of metal pollution emitted from the Giant Mine during the 1950s. Paleohydrological knowledge was, thus, also key to applying this novel approach for assessment of pollution from both oil sands development and Giant Mine emissions, as further discussed below.

4.2. Assessment of metal pollution from the Alberta oil sands industry

Community concerns in the SRD regarding pollution from the Alberta oil sands development have been mounting in response to previous research that has documented evidence of enhanced atmospheric deposition of heavy metals and PACs within a radius of at least 50 km from a defined center of the bitumen-upgrader facilities at the Alberta oil sands (Kelly et al., 2009, 2010; Kurek et al., 2013; Kirk et al., 2014). Such concerns were the impetus for this study. However, post-1967 (since onset of oil sands development) metal concentrations in both high flood and low flood influence intervals from lake SD2 align with the determined pre-1967 baseline concentrations. Of the 336 post-onset oil sands development samples measured in the SD2 stratigraphic record, only eight (~2.38%) exceeded the 95% PI. For all metals except As, concentrations in sediments deposited after onset of oil sands development were below the Interim Sediment Quality Guidelines for the Protection of Aquatic Life for those metals where this has been established, which include: Cd (0.6 mg kg^{-1}), Cr (37.3 mg kg^{-1}), Cu (35.7 mg kg^{-1}), Pb (35.0 mg kg^{-1}), Hg (0.17 mg kg^{-1}) and Zn (123.0 mg kg^{-1}) (CCME, 2014). Arsenic exceeded the threshold concentration (5.9 mg kg^{-1}; CCME, 2014) in the majority of samples deposited both before and since the onset of oil sands development. Therefore, we conclude that sediment metal concentrations at SD2 have not been enriched by the Alberta oil sands development above baseline concentrations. Instead, results indicate that accumulation of metals has occurred at SD2 via natural processes of fluvial transport and deposition for at least the past 90 years.

Higher metal concentrations post-1967 (except As), evident in both the stratigraphic plots (Fig. 4) and from independent sample t-tests, clearly point to the need to normalize metal concentrations to account for confounding influence of variations in past hydrological conditions, and the need to determine pre-industrial baseline concentrations. Without such knowledge, it is impossible to evaluate time series of sediment metal concentrations for evidence of pollution due to human activities, especially in depositional settings subject to fluctuations in the influence of hydrological processes. For example, one might incorrectly associate the apparent rise in bulk metal concentrations in post-1967 samples to pollution from oil sands development, but the difference is most likely a function of increased occurrence of finer-grained

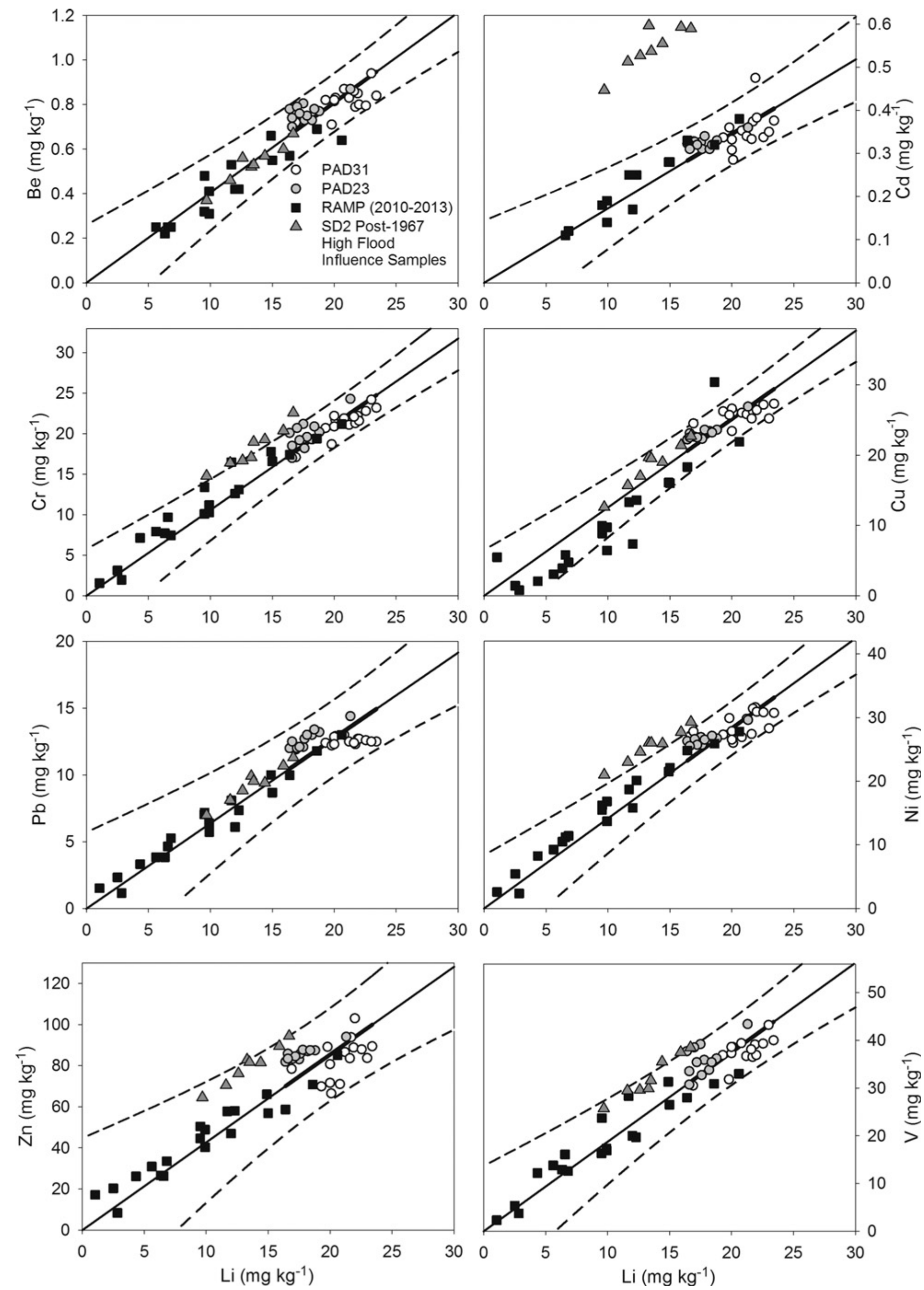

Fig. 8. Scatterplots showing Li-normalized metal concentrations in sediment samples from lake SD2 deposited post-1967 during intervals of high flood influence superimposed on pre-industrial baseline (solid lines) and 95% prediction intervals (dashed lines) constructed for the Athabasca Delta from analyses on sediment cores from lakes PAD23 and PAD31 (from Wiklund et al., 2014). Also shown are RAMP (Regional Aquatics Monitoring Program) data from surficial river sediment samples taken from downstream Athabasca River and Delta stations, as reported in Wiklund et al. (2014).

sediments deposited during intervals of lower flood influence, a consequence of climate-driven change in the runoff regime of the upper Mackenzie River Basin (Brock et al., 2010).

While lack of evidence for enhanced metal deposition associated with oil sands development at SD2 is consistent with findings in the PAD, which have assessed both fluvial and atmospheric pathways (Wiklund et al., 2012, 2014), absence of high flood influence deposits in the most recent strata, which corresponds to a time of accelerated growth in the oil sands industry, does impose some limitations to our findings. Yet, some of the metals contained in the SD2 record delivered by fluvial pathways appear to be derived from elsewhere in the watershed, based on superimposing metal-Li concentrations in post-1967 high flood influence sediments from SD2 on the baseline metal-Li relations developed by Wiklund et al. (2014) for river sourced-sediment in the Athabasca Delta (Fig. 8). Li-normalized concentrations for Cd, Cr, Ni, Zn and V in sediments from SD2 consistently plot along unique trajectories at or just above the 95% PIs defined for these metals at the Athabasca Delta, suggesting that SD2 receives metals from sources that are enriched relative to those that supply the Athabasca River. A probable source is the Peace River, which contributes two-thirds of Slave River discharge. Differences in surficial geology of the watersheds of these rivers, including outcrops of coal seams in the

Peace watershed identified as a possible source of PACs that enter the northern Peace sector of the PAD during flood events (Jautzy et al., 2015), likely account for the differences in metal-Li relations in lake sediments at the SRD and the Athabasca Delta. These findings demonstrate that baseline metal concentrations established at one location by paleolimnological methods may not be directly transferrable to other landscapes, but they can be used to detect other potential sources of metal deposition.

4.3. Assessment of As pollution during the 1950s

Although not the original intent of this study, elevated As concentrations identified during the extremely low flood influence interval of the 1950s at SD2 necessitated further exploration. Assuming deposition via atmospheric pathways, and when plotted against baseline concentrations as determined from low flood influence intervals pre-1950 and post-1960, four samples had unusually high As concentrations (~1954, ~1955, ~1957 and ~1959; Fig. 7). After ~1959, As concentrations decrease rapidly and return to baseline concentrations. These results indicate an additional source of As was deposited at SD2, and likely directly on the lake surface, during the 1950s.

At this time, the Giant Mine in Yellowknife (NWT) developed rapidly (Hocking et al., 1978; Fig. 1). The gold deposit at Giant Mine is composed of arsenopyrite ore (AANDC, 2013). To convert the arsenopyrite to roaster calcine and then to gold, highly toxic As vapor was released as a by-product. Arsenic pollution from Giant Mine has long been a concern for the city of Yellowknife. Consequently, many studies have assessed As in water, sediment, soil, snow, plants and animals in the Yellowknife region and found elevated concentrations (e.g., Hutchinson et al., 1982; Murdoch et al., 1989; Bright et al., 1996; Jackson et al., 1996; Koch et al., 2000; Andrade et al., 2010; Bromstad, 2011). However, to our knowledge, no studies have assessed or identified As pollution from Giant Mine at more distant locations. Peak sediment As concentrations (19.1 mg kg^{-1}) at SD2 exceeded our defined baseline concentrations, as well as CCMEs Probable Effects Level (17.0 mg kg^{-1}). The timing of the As concentration peak at SD2 is consistent to within ~5 years of maximum reported emissions from Giant Mine (Hocking et al., 1978; Fig. 9). Furthermore, sediments containing the As peak were also high in Sb, Ca and Sr concentrations (Ca and Sr data not shown), which are major volatile elements within the mineralogy of the Giant Mine ore deposit (arsenopyrite, stibnite within quartz–carbonate veins; Silke, 2013). Collectively, these findings suggest our extrapolation of the linearly-estimated sedimentation rate to produce the sediment core chronology is reasonable.

In 1958, a two-stage roaster was installed to improve efficiency and recovery of pollutants, and a baghouse was constructed to reduce emission rates (Bromstad, 2011; AANDC, 2013). After these measures were undertaken, As emissions from Giant Mine decreased markedly and this appears to be captured by rapid decline of As concentration to baseline levels in the SD2 sediment record. We note that the timing of maximum As pollution from Giant Mine occurred during very low water levels at SD2. Absence of dilution of sediment-As concentrations by As-poorer sediment from Slave River floodwaters provided the ideal hydrological conditions for atmospheric transport of pollution to be archived in the stratigraphic profile at this location. Given that Giant Mine is the closest major source of As emissions and the timing of peak sedimentary As concentrations at SD2 closely coincides with peak emissions from that mine, our findings suggest pollution from Giant Mine extended at least ~140 km to the south of Yellowknife.

Far-field As pollution from Giant Mine may also be evident in the PAD, given that it is likely the closest major point source of As emissions (Fig. 9). Peak concentrations in residual As have similar timing, despite lower values in lake 'PAD18', an elevated precipitation-fed lake situated ~20 km north of the town of Fort Chipewyan in the Peace Delta (Wiklund et al., 2012) and ~430 km south of Giant Mine. By the late 1950s, residual As concentrations in PAD18 also decreased, but more gradually than observed in SD2. The gradual decline in PAD18 versus the sharp decline in SD2 may reflect the very different hydrological settings of the two basins. While emissions declined, a return to high flood influence may have substantially diluted the As concentrations at SD2 with river-transported sediment from unaffected areas, leading to an abrupt decline in the As stratigraphic record. In contrast, PAD18 remained precipitation-fed and perhaps more accurately portrays reduction in atmospheric transport of As emissions from Giant Mine. Although the SRD and PAD are ~140 and ~430 km from Giant Mine, respectively, the very high As emissions from Giant Mine during the 1950s (~15,178 long tons ~1949–1958; Hocking et al., 1978) may very well have been transported far afield. For instance, a base metal smelter in Flin Flon (Manitoba) emitted 2783 t (2485 long tons) of As from 1931 to 1974 and As pollution was identified up to 104 km from the smelter (McMartin et al., 1999). Given the much higher emissions at Giant Mine compared to Flin Flon, it is reasonable for As pollution to reach similar and even greater distances than reported in McMartin et al. (1999).

5. Conclusions

Paleohydrological reconstruction based on measurements made on a sediment core from a flood-dominated lake in the Slave River Delta provided necessary context to develop baseline concentrations of metals delivered by fluvial and atmospheric pathways for assessing pollution from regional mining point sources. Since onset of Alberta oil sands development (post-1967), concentrations of metals in both high and low flood influence intervals, normalized to Li to account for expected variations in grain size and mineralogy, were within the natural range of variability defined by pre-1967 high flood influence interval metal concentrations. These results indicate that oil sands development has not yet enriched sediment metal concentrations above natural levels conveyed by Slave River floodwaters to lake SD2. Indeed, our study demonstrates that metals have naturally accumulated in the SRD for at least ~90 years, although greater concentrations are found during intervals of low flood influence, which may reflect deposition of finer-grained sediments that are remobilized from the lake's local catchment. Comparison to baseline metal-Li relations developed for the lower Athabasca River reveal that fluvial-derived metals in SD2 sediments may in fact be from other source(s) in addition to the Athabasca River. Erosion of metal-bearing deposits along the Peace River is a likely source because the Peace River supplies two-thirds of the Slave River's flow. Importantly, our analysis revealed elevated As concentrations were captured in the lake sediment record during the 1950s when water levels were extremely low at SD2 and floods were not frequent, suggesting transport from a source of pollution via the atmosphere. Residual As, calculated after defining background Li-normalized As concentrations from pre-1950 and post-1960 low flood influence intervals, corresponded well with As emission history from Giant Mine, located ~140 km to the north, suggesting a much broader atmospheric pollution footprint during the early phase of mine operation than has previously been recognized. Despite the dynamic nature of floodplain lakes, knowledge of past hydrological conditions can effectively inform multiple pathways and processes of contaminant deposition, as needed to identify sources of pollution.

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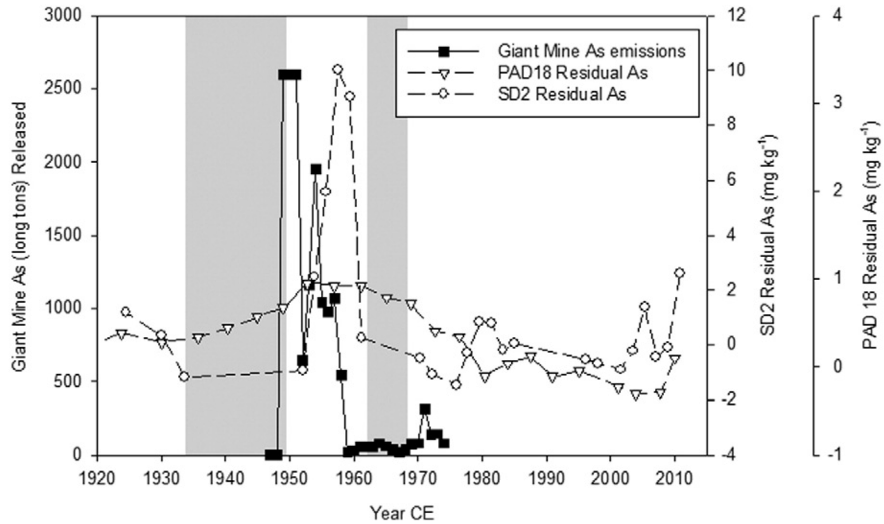

Fig. 9. Comparison of As emissions from Giant Mine as supplied by the company and by Northwest Region, Environmental Protection Service and reported in Hocking et al. (1978), with the temporal pattern of change in residual As concentration in sediments from lakes SD2 and PAD18 (Wiklund et al., 2012). SD2 residual As concentrations were derived from the As–Li relation of low flood influence samples from pre-1950 and post-1960 (Fig. 7). PAD18 residual As concentrations were derived from analysis of As and organic matter from samples deposited pre-1900. Vertical gray bars represent intervals of high flood influence at SD2 that bracket the ~1950s.

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